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Long-Term Persistence of Picloram in a Sandy Loam Soil[1]

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ABSTRACT

Picloram (4-amino-3,5,6-trichoropicolinic acid) was applied to a ryegrass (*Lolium perenne* L. cv S23) sward at 0.05, 0.28, and 1.68 kg ai (active ingredient)/ha in June 1967 and again in August of 1969 and 1970. Small amounts of residue were found in soil samples 1 year after application of the low and medium doses. On the highest dose plots 5 to 6% of the amount applied was usually recovered 1 year after spraying. Following the final application this residue degraded slowly over the following 3 years. Analyses of the final samples (taken 222 weeks after spraying) indicated that the residue had declined to about 0.5% of the total amount applied. In stratified soil samples, residues were found to the maximum sample depth of 90 cm 1 year after the initial application, but 69 weeks after the final application no residue was found below 30 cm.

Crops grown across all plots in 1974 did not differ in yield. However, on the plots that had received the highest dose, leaf abnormalities were noted in beans and potatoes and color differences were observed in kale.

Additional Index Words: **Tordon, United Kingdom, herbicide leaching, phytotoxicity.**

Picloram (4-amino-3,5,6-trichloropicolinic acid) is one of the most effective herbicides for dicotyledonous species, but its use is restricted in cropped land because of its persistence in soil at levels which are phytotoxic to certain crops. It is potentially mobile, falling into mobility class IV of Helling (1971). At the time this experiment began, picloram was marketed in the United Kingdom (UK) for use in cereals, in grassland, and in noncrop areas. Little was known of the persistence and phytotoxicity of repeated applications or its movement in the soil profile under UK conditions.

METHODS AND MATERIALS

The experiment was begun in spring 1967 at the Weed Research Organization (WRO) on a well-draining sandy loam soil which is 0.7 to 1.2 m deep including subsoil, overlying gravel. The average mineral composition is: coarse sand, 43%; fine sand, 20%; silt, 24%; clay, 13%. The organic matter content in 1967 was 2%. Only traces of $CaCO_3$ were detectable, but the pH value was 7. The mean annual rainfall during the course of the experiment was 65.3 cm, the long-term annual mean being 61.8 cm.

The experimental area was plowed in January 1967 and prepared for seeding in early spring. Perennial ryegrass (*Lolium perenne* L. cv. S23) was drilled in 30-cm rows on 4 April to provide ground cover. It was mown periodically, the cut foliage being left on the plots.

The experiment was designed as three randomized blocks, each consisting of four plots, 18.3 by 4.6 m, separated by 2.7-m wide paths. Three plots received picloram K salt applications of 0.05, 0.28, and 1.68 kg ai/ha. The fourth was untreated. The rates used correspond approximately to those recommended in the UK for use in cereals, in grassland, and in noncrop areas at the time the experiment was started.

The initial picloram application, made on 14 June 1967, was followed by two further treatments on 5 Aug. 1969, and 2 Aug. 1970. It was originally intended to spray annually but this was not possible due to staffing problems. Applications were made with the Oxford Precision Sprayer at a volume rate of 240 liters/ha.

Immediately after each spraying 20 soil cores (2.5 by 15 cm) were taken from each plot. Further samples were taken prior to each spraying and at various intervals when 10 cores per plot were taken with a 4.5-cm-diam split-tube corer which allowed the soil core to be laid open and divided into horizons. For the deepest sampling (down to 1.5 m), which was only carried out on the high-dose plots, a 5-cm-diam Dutch auger was used; ten 15-cm horizons were collected at each of five sampling points in each replicate. To prevent contamination of the lower horizons with surface soil, the surrounding area (a minimum of 30 by 30 cm) was cleared by spade to the top of the horizon to be sampled. Samples from each depth were bulked, separately for each plot, and stored at −18°C. When required, they were thawed, passed through a 3-mm mesh, mixed, air-dried at room temperature, and analyzed for picloram.

Sampling schedules and depths will appear somewhat erratic. There was a shortage of field and laboratory staff during the experiment and a wane of interest in picloram following its withdrawal from use in the UK. This prompted decisions to reduce sampling frequencies and to confine sampling depths to the top 15 or 30 cm where residues would have an effect on subsequent crops.

In the first 2 years residues were determined by bioassay using dwarf bean (*Phaseolus vulgaris* L.). Assessments were made 4 weeks after sowing by visual scoring on a 0 to 9 scale. The standard series of soil samples contained 0.80 to 500 ppb picloram and samples from the field plots were diluted with control soil so as to fall in this range. After 1968 the gas-liquid chromatographic (GLC) method subsequently reported by McKone and Cotterill (1974) was used. The limit of detection of the bioassay was 0.8 ppb and that of the GLC method was 1.0 ppb. Concentrations in ppb were corrected to g/ha using conversion factors derived from soil bulk density which varied from year to year.

Precipitation, evaporation, and transpiration all affect the availability of water to aid herbicide degradation and movement in the soil. The amount of water loss from the soil due to transpiration is not known, but the figures for precipitation and the evaporation from a free water surface can give an indication of the water availability in the soil. These data were collected at the WRO meteorological station. During the two 5-mo overwintering periods (1967–68 and 1968–69) the evaporation readings were discontinued. Calculations for the probable evaporation for these times were made according to the method of Penman (1948).

In the final year (1974), the whole area was plowed, cultivated, and sown in strips across the plots with barley (*Hordeum sativum* Jess cv. Julia), potatoes (*Solanum tuberosum* L. cv. King Edward), field beans (*Vicia faba* L. cv. Maris Bead), kale (*Brassica oleracea* L. cv. Maris Kestrel), and lettuce (*Lactuca sativa* L. cv. Borough Wonder). Regular checks were made on all plots during the growing season and any visual differences noted. Plant growth and yield were assessed as appropriate.

RESULTS

Residue Assessments

A summary of picloram recovered from the soil throughout the experiment together with precipitation and water evaporation figures is presented in Table 1. Immediate post-spray recoveries on the 280-g/ha plots in 1969 and on the 50- and 280-g/ha plots in 1970 were very low (approximately 50%). We cannot suggest an

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Table 1—The persistence of picloram applied repeatedly to a sandy loam soil.

Date of spraying	Weeks after spraying	Precipitation since initial application	Evaporation from free water surface since initial application	Depth of soil samples	Total residue recovered						Method of determination
					dose 50 g/ha		dose 280 g/ha		dose 1,680 g/ha		
		cm			g/ha	SE	g/ha	SE	g/ha	SE	
6/14/67	0	0	0	0-15	35.8	†	279.6	†	1,455.1	†	Bioassay
	2	2.9	3.9	0-15	26.0	†	130.0	†	896.0	†	Bioassay
	52	88.1	64.0	0-90	--	--	6.7	0.45	96.4	100.5	Bioassay
	52	88.1	64.0	0-110	0.89	0.33	--	--	--	--	Bioassay
	96	140.2	145.7	0-75	--	--	--	--	82.0	31.9	Bioassay
8/ 5/69	0	159.7	176.5	0-15	37.8	2.5	163.8	23.3	1,182.3	6.9	GLC§
	50	207.7	224.5	0-15	14.1	0.7	16.8	2.1	89.7	22.3	GLC
8/ 2/70	0	209.0	226.7	0-15	25.2	2.5	136.5	4.8	1,610.7	69.9	GLC
	37	249.4	251.3	0-15	9.0	1.7	12.0	1.4	--	--	GLC
	37	249.4	251.3	0-30	--	--	--	--	80.4	3.7	GLC
	69	297.4	298.5	0-15	7.8	0.7	11.1	0.7	--	--	GLC
	69	297.4	298.5	0-150	--	--	--	--	84.6	9.5	GLC
	120	346.8	364.4	0-15	--	--	--	--	42.0	3.2	GLC
	162	390.1	405.7	0-15	--	--	--	--	18.9	5.3	GLC
	222	462.4	461.2	0-40	--	--	--	--	23.2	‡	GLC

† All values identical within the limitation of the scoring system used.
‡ All values identical.
§ Gas liquid chromatography.

explanation. Reasonable recoveries in the other cases, combined with laboratory studies, confirm that the extraction method was effective.

Stratified soil samples were taken on several occasions on the high dose plots. Fifty-two weeks after the initial application, samples, when bioassayed, showed small amounts of the residue to the maximum sample depth of 90 cm. No residue was found below 30 cm at the last sampling of these plots, to the depth of 150 cm, 69 weeks after the last application (Table 2).

Since the low residue on the high-dose plots 1 year after the final application still represented an appreciable quantity of picloram, soil sampling and analysis was continued at intervals until 222 weeks after the final application, when about 25 g/ha per 40 cm was present.

Field Phytotoxicity Assessments in 1974

Bean plants growing on the high-dose plots showed varying degrees of leaf roll above the seventh node (Fig. 1) as early as 1 July. An assessment was made on 6 September (Table 3). This condition persisted through the growing season but the yield of beans was not affected. Plants on low- and medium-dose picloram plots were not distinguishable from controls.

The youngest potato leaves were seen to be constricted, shortened, and crinkled on 16 July (Fig. 2). Again this effect was noted only on the high-dose plots (Table 3). It continued for the remainder of the season, but the yield of tubers was unaffected.

No differences occurred on the lettuce plants, and they were removed after they matured in mid-July.

The kale on the high-dose plots was lighter in color than the controls from 5 August. An assessment was made on 13 September (Table 3). This visual symptom, like the others, persisted until harvest with no effect on the final yield.

As expected, no visible symptoms appeared on the barley. There were no differences in leaf number, plant height, or yield on any of the barley plots.

Table 2—Picloram residues in soil horizons following applications at 1,680 g/ha.

Horizon depth	52 weeks after 1st spray		96 weeks after 1st spray		50 weeks after 2nd spray		37 weeks after 3rd spray		69 weeks after 3rd spray	
cm	g/ha	SE	g/ha	SE	g/ha	SE	g/ha	SE	g/ha	SE
0-15	24.8	7.7	35.8	--†	79.8	9.9	65.1	2.7	75.6	6.3
15-30	26.0	37.6	25.6	18.1	10.1	2.4	15.3	1.8	9.0	4.6
30-45	2.6	3.1	17.2	18.6	ND‡		ND		<2.1	--†
45-60	2.5	4.1	2.7	0.55	ND		ND		<2.1	--†
60-75	12.1	17.2	1.7	0.87	ND		ND		<2.1	--†
75-90	28.5	49.2	ND		ND		ND		<2.1	--†
90-150	ND		ND		ND		ND		<2.1	--†
in 15-cm horizons										

† All values equal within the limitations of the method used.
‡ ND = not determined.

DISCUSSION

Approximately 1 year after each application between 2 and 6% of the picloram applied was recoverable (with the exception of the low-dose plots which contained up to 28%). The picloram remaining on the high-dose plots 1 year after the final application (1.7% of the total

Fig. 1—Field bean plants showing the leaf roll effects observed on the high dose plots 4 years after the final application.

Table 3—Effects of residual picloram on test crops in 1974 following picloram treatments in 1967, 1969, and 1970.

Crop/assessment	Dose picloram, kg/ha			Untreated control
	0.05	0.28	1.68	
% bean plants showing leaf curl symptoms on 6 September	0	0	100***	0
% potato leaves showing constriction symptoms on 6 September	0	0	33***	0
Mean score for kale color, 13 September Greenest control = 10 No color = 0	8.8	9.0	7.2**	9.5

,* Significant at the 0.01 and 0.001 levels, respectively.

amount applied) decreased very slowly over the following 3 years. Ragab (1974) found 35% of a 4.48-kg/ha application remained after 48 weeks (73.6 cm precipitation) in a sandy loam soil in Canada. Goring et al. (1965) reported persistence from a 1.68-kg/ha application at several sites in the United States ranging from only 4% after 5 mo to as much as 17% after 28 mo.

In field studies of herbicide persistence in soil in the Philippines and South Vietnam where 1.81 kg/ha picloram was applied, no residue was detected by sensitive crops or by chemical analysis 1 year later (U.S. Natl. Acad. of Sci., 1974).

The results show that there was no accumulation of picloram residue in the sandy loam soil despite the repeated application. This contrasts with Hunter and Stobbe (1972) who found that accumulation did occur after two annual applications of 350 g/ha on a heavy clay soil, but the difference in soil type may account for this.

Picloram determination by bioassay gave highly variable results in some cases (Table 2). Fifty-two and ninety-six weeks after the first application (after 88 and 140 cm precipitation, respectively) picloram was detected to the maximum sample depth (90 and 75 cm, respectively) but, because of the high standard errors, the figures must be regarded as unreliable. Sixty-nine weeks after the final application (88 cm precipitation) no residue was found below 30 cm. Overall evaporation was very similar to precipitation and daily rainfall exceeded 30 mm only five times during the whole period of the experiment. Therefore, it is unlikely that there was any considerable leaching loss below the sampled depth. Comparison with other work is difficult because figures for evaporative water losses have rarely been reported. Hunter and Stobbe (1972) report that movement is negligible at low levels of soil moisture but found residues down to 60 cm after heavy rainfall. Herr et al. (1966) found that downward movement was small in heavy clay soils with a high organic matter content and very fast in light soils with low organic content. Scifres et al. (1969) found in addition that movement of picloram to the 60- to 90-cm horizon was evident from 1 to 3 years after treatment, indicating downward movement to the subsoil. The greatest dissipation rate was in the upper 30 cm.

Fig. 2—Potato plants showing leaf constriction and crinkling observed on the high dose plots 4 years after application.

Phillips and Feltner (1972) detected phytotoxic residues near the surface only at one silty clay loam site after five annual applications of 2.24 and 3.36 kg/ha picloram. At another site they found residues to a depth of 2.4 m after a single application. Baur et al. (1972) found residues down to 2.4 m 6 mo after the application of 1.12 kg/ha picloram to a fine sandy loam overlying dark clay (during which time there was 39.1 cm of precipitation).

The yield of crops grown in the final year was not affected by the picloram, but the leaf abnormalities indicated that herbicide had been taken up. No picloram analyses were carried out on plant material but, when the results of the soil analyses are considered together with the toxicological details in the Tordon (picloram) information manual (Dow Chemical Co., 1963), it is most unlikely that the residues in the plant would be toxic to animals.

Where visual symptoms were seen they ended sharply at the edge of the plot, suggesting that lateral movement of picloram did not take place. Byrd et al. (1971), using picloram and 2,4-D triisopropanolamine salts, found that there was very little picloram movement from the edge of the spray swath and that surface run-off from rainfall immediately after spraying was the probable cause of any lateral movement that did take place.

CONCLUSIONS

Under the conditions of this experiment, no accumulation of picloram took place, there was little lateral movement of residue in the soil, and after an initial fast disappearance only a slow disappearance of the remaining small but active residue took place over several years. Morphological differences in crops grown in soil containing picloram residue do not necessarily indicate yield loss.

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